A study of chemically and biologically synthesized dual doped titanium dioxide (TiO_2) nanoparticles

SYNOPSIS

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1. Introduction

1.1. Nanotechnology

The engineering of the material particles at their atomic level more specifically at the nanometer size to achieve the unique properties, which can be suitably manipulated for the desired applications, is the study of a well-known field called nanotechnology (Virkutyte & Varma, 2013). Nanotechnology is the study of manipulating matter on an atomic scale. Nanotechnology refers to the constructing and engineering of the functional system at very micro level or we can say at atomic level. A nanometer is a unit of length in the metric system, equal to one billionth of a meter (10^{-9} m or 1 nm) whereas technology is the making, usage and knowledge of tools, machines and technologies in order to solve a problem or perform a specific function (Khandelwal & Joshi, 2018). The first ever concept was presented in 1959 by the famous professor of physics Dr. Richard P. Feynman (Tarafdar, Sharma & Raliya, 2013). The term "Nanotechnology" had been coined by Norio Taniguchi in 1974 (Subedi, 2013).

1.2. Nanoparticles (NPs)

NPs have become a prominent nanomaterial in today's growing world due to their existing chemical, physical and biological properties. NPs are tiny particles with a size range of 1 to 100 nm in one dimension made from metals, metal oxides, carbon, or other organic materials (Balkrishan et al., 2021). It exhibits a unique property at nanoscale due to its relatively large surface area to volume ratio, chemically stability, high reactivity, intensive mechanical strength, etc., (Anu et al., 2020).

1.3. Titanium Dioxide (TiO_2)

In 1821, TiO_2 was discovered and considered one of the best inorganic compounds used at industries level. TiO_2 is an inorganic substance of white solid which is non-flammable, thermally stable and insoluble substance. TiO_2 is the 9^{th} common element in the earth crust, occurring naturally in different types of rocks and sands (Riyas, Yasir & Das, 2002). It is 4^{th} group element in the periodic table and shows four valence properties. Additionally, it shows di (TiO) and trivalent (Ti_2O_3) valence states. TiO_2 is also known as titania, and it is mostly utilized as a white pigment due to its high refractive index and brightness (Roy, Berger & Schmuki, 2011). Titania acts as semiconducting materials due to its stable pH range, chemical inertness, non-toxic and band edge deposition. The crystalline state of TiO_2 powder has a growing interest in novel applications in medical

science. The application of TiO_2 does not depend upon its properties only but also depends upon the state of TiO_2, either crystalline or amorphous form (Yangi & Wu, 2012).

TiO_2 exists in only two forms: amorphous and crystalline. It is classified into three states: Anatase, Rutile and Brookite. TiO_2 is classified based on its physical features such as surface area, optical band gap, and so on (Keskin et al., 2020). The anatase has tetragonal structure that acts as photocatalysts. It shows very high photocatalytic properties and the rutile is used as a white pigment in paints. In the TiO_2 crystalline form, the Ti^{4+} ion is encircled by the octahedron oxide ions. In anatase phase, each octahedron ions in commerce with eight neighbour octahedrons (four oxygen pairs at edge and four oxygen atoms that share a corner). It is explained by the TiO_6 octahedron chain in which six octahedron O^{2-} ions cover each Ti^{4+} ion. The variance in the structure of anatase is the octahedron chain assembly pattern and distortion of each octahedron (Wang et al., 2014).

1.4. Polyvinylpyrrolidone (PVP)

PVP a flexible polymer composed of vinylpyrrolidone units, boasts a wide array of applications across diverse industries, thanks to its distinct characteristics. Its exceptional solubility in water and various organic solvents renders it invaluable in pharmaceuticals, cosmetics, and industrial sectors (Kim et al., 2021). In pharmaceuticals, PVP acts as a crucial excipient, enhancing drug solubility, bioavailability, and stability. It finds common usage in tablet coatings, granulation processes, and as a binder in solid dosage forms. Within the cosmetics realm, PVP is celebrated for its ability to form durable films, making it a staple ingredient in hair styling products like hairsprays, gels, and mousses. These films offer enduring hold and style retention (Ahmad et al., 2019). Moreover, PVP is employed across industrial processes, including adhesives, textiles, and ceramics. Its adhesive properties make it ideal for glue formulations, while its capacity to improve dye absorption and dispersion makes it indispensable in textile dyeing processes. Overall, PVP's versatility and distinctive properties position it as a fundamental polymer in numerous applications, playing an essential role across global industries (Shepa et al., 2020).

1.5. *Tinospora Cordifolia (T. Cordifolia)*

Natural products with medicinal value are gradually gaining importance in clinical research due to their well-known property of no side effects as compared to drugs. *T. Cordifolia* commonly named as “Guduchi (Giloy)” in Sanskrit belonging to family Menispermaceae is a genetically diverse, large, deciduous climbing shrub with greenish yellow typical flowers, found at higher altitude (Upadhyay et al., 2010). In racemes or

racemose panicles, the male flowers are clustered and female are solitary. The flowering season expands over summers and winters (Parthipan, Aravindhan & Rajendran, 2011). A variety of active components derived from the plant like alkaloids, steroids, diterpenoid lactones, aliphatic and glycosides have been isolated from the different parts of the plant body, including root, stem and whole plant. *T. cordifolia* has an importance in traditional ayurvedic medicine used for ages in the treatment of fever, jaundice, chronic diarrhea, cancer, dysentery, bone fracture, pain, asthma, skin disease, poisonous insect, snake bite, eye disorders (Upadhyay et al., 2010). Such properties may be exploited for production of new formulations, which may be better and promising over conventional one.

1.6. Doping

Metallic oxides are frequently doped to increase their electrical, optical and catalytic properties. The prime mechanism in the back of such property is to govern doping that alters the characteristics of transferred electrons via changes in crystalline structure (Buonsanti and Milliron, 2013). There are numbers of transition metals used as dopants to change the physical and chemical properties of TiO_2 nanostructures or NPs. When doped with transition metals, it creates a level of impurity between the conductive and valence band, which serves as an intermediate step to relieve the electron during photon absorption excitation. Such levels of impurity can be known as levels of acceptors, deep recombination centers and shallow donors. Therefore, these enough deep defect states support recombination centers of excitons i.e. electron (e^-) and hole (h^+) (Pelaez et al., 2012). Surface modification of TiO_2 NPs provides greater benefits than bulk TiO_2 alteration because fundamental goal of doping is to narrow the bandgap, which causes visible light to be emitted and preferable to keep same crystal structure of TiO_2 while changing its electrical composition through doping (Burda et al., 2003). A number of researches have attempted doping of TiO_2 nanostructured materials but it still remains a challenge to achieve high quality of crystalline material with excellent physical and chemical properties of doped TiO_2 nanostructures (Carp et al., 2004).

2. Literature Review

Khade et al. (2016) synthesized Samarium (Sm) doped TiO_2 NPs by microwave assisted sol-gel method. It is also found that the crystallite size of Sm doped TiO_2 is much smaller than undoped TiO_2 (10 nm). The photocatalytic activity of TiO_2 and Sm doped TiO_2 were also investigated on the photocatalytic degradation of Methyl Orange under UV

and solar light irradiation and showed 96 and 84 % in 120 min under UV light and sunlight respectively.

Kashale et al. (2016) used simple, green and cost-effective method for the synthesis of TiO_2 NPs, wherein remnant water (ideally kitchen waste) collected from soaked Bengal gram beans (*Cicer arietinum L.*) extract is reacted with $TiCl_4$. Biosynthesized TiO_2 (Bio-TiO_2) NPs with uniform size distribution were obtained as a result of the stabilizing molecules naturally present in the extract. The morphology, crystal structure and phase composition, specific surface area and pore size distribution of Bio-TiO_2 were systematically investigated by XRD (X-Ray Diffraction), Raman spectroscopy, Transmission Electron Spectroscopy (TEM), thermogravimetric analysis (TGA) and BET surface area measurement system. Li-insertion properties were evaluated as anodes in the half-cell configuration (Li/Bio-TiO_2) and it is found to demonstrate reversible insertion of 0.61 mol at a current density of 33 mA g^{-1}.

Kadam et al. (2017) synthesized Tin (Sn) doped Nitrogen (N)-TiO_2 NPs with different contents of Sn by a greener microwave assisted method. The phase purity, morphology, particle size, optical properties and elemental composition were systematically analyzed by various sophisticated analytical techniques. XRD patterns revealed Sn doped N-TiO_2 NPs in the anatase phase. The optical absorption edges of Sn-doped N-TiO_2 showed an obvious red shift that plays a crucial role in the photocatalytic activity under abundant sunlight. Sn doped N-TiO_2 were explored for photodegradation of MO and Zopiclone (Z-class drug) under sunlight irradiation. A maximum of 95 and 91 % of MO and Zopiclone were photodegraded over 0.25 % Sn doped N-TiO_2 under sunlight within 80 and 120 min, respectively, which is ~7-fold higher than bare N-TiO_2.

Dobrucka (2017) biosynthesized the TiO_2 NPs using an aqueous solution of *Echinacea purpurea herba* extract as a bioreductant. The prepared TiO_2 NPs were characterized using various characterization techniques. The size of TiO_2 NPs was found to be in the range of 120 nm. Moreover, the alkaline reaction of the solution (pH = 8) resulted in the increase in absorbance (280 nm), which facilitates the growth of the number of TiO_2 NPs in the studied solution.

Oseghe and Ofomaja (2018) synthesized pine cone derived carbon doped TiO_2 materials via facile microwave procedure at different powers, different from other conventional synthesis methods. The materials were adequately characterized and applied in the photodegradation of 5 mg/L tetracycline hydrochloride (TA) under visible-LED light. The composite material synthesized at a microwave power of 800 W (CT800),

displayed the highest band gap energy (3.14 eV) but showed the least electron-hole recombination rate. Hence, CT800 exhibited the highest apparent rate constant of 9.9×10^{-3} min^{-1} and a half-life of 70 min. An inverse relationship between OH^- radical scavenger (isopropanol) and the percentage degradation by CT800 suggests that OH^- is majorly responsible for the degradation of TA. Recyclability studies revealed that after 4 cycles of photocatalytic degradation reactions, CT800 retained approximately 83 % performance confirming its stability and reusability.

Subhapriya & Gomathipriya (2018) biosynthesized the TiO_2 NPs by chemical and biosynthesized method using the aqueous leaf extract of *Trigonella foenum-graecum* (TF). The XRD displayed the existence of TF-TiO_2 NPs which is confirmed by the incidence of peaks at 25.28 corresponds to 101 anatase form. SEM perceptions revealed that synthesized TiO_2 NPs were spherical in shape and the size of individual NPs as well as a few aggregates was found to be 20-90 nm. The antimicrobial activities of biosynthesized NPs (TF-TiO_2 NPs) were examined using Kirby-Bauer method. The TF-TiO_2 NPs showed significant antimicrobial activity against all the tested microorganisms.

Andrade et al. (2019) synthesized Boron (B) doped TiO_2:xB (x = 0, 1, 2, 4 and 8 mol. %) by using microwave-assisted solvothermic method at 140 °C for 10 min. The NPs obtained were characterized by XRD, FTIR, Raman spectroscopy, photoluminescence, SEM and diffuse optical reflectance. The photocatalytic properties were estimated against methylene blue dye. The XRD patterns show that there was no formation of secondary phases and that all the peaks correspond to the anatase phase of TiO_2. Rietveld's refinement showed that the addition of B^{3+} in the TiO_2 lattice promotes a reduction in the size of the crystallites and this reduction it effectively increases the degradation capacity of the methylene blue dye, which after 50 min the 8 % B sample degraded completely, while the pure TiO_2 sample reduced its concentration by 95 %. B-doped TiO_2 was effective when reused and after the third cycle the photocatalytic activity of the powders was maintained. In addition, the incorporation of 8 % B in the TiO_2 lattice resulted in an increase from 8.66 to 15.61 mm and 9.04 to 13.65 mm in the inhibition halos of the *S. aureus* and *E. coli* bacteria, respectively.

Abisharani et al. (2019) reported that bio synthesized method has received great attention in recent years due to its capability to design alternative, safer, energy efficient and less toxic routes towards synthesis. These routes have been associated with the rational utilization of various substances in the NPs preparations and synthetic methods. They described the green synthesis of TiO_2 NPs from titanium try chloride ($TiCl_3$) solution using

Cucurbita pepo seeds extract. The synthesized TiO_2 NPs were characterized XRD, UV-VIS, FT-IR spectroscopy.

Ismael (2020) prepared bare TiO_2 and different molar concentrations of iron (Fe^{3+})-doped TiO_2 photocatalysts (0.05-1 mol % Fe) by a simple precipitation method for photocatalytic hydrogen production and degradation of organic pollutants methyl orange (MO) under light irradiation of $\lambda \geq 320$ nm. XRD revealed the presence of anatase phase for both bare TiO_2 and Fe doped titania. N_2 adsorption results showed that the doped materials have higher surface area compared to bare TiO_2 due to decrease particle size. Also, electrochemical experiments (electrochemical impedance spectroscopy (EIS), photocurrent (PC), and photoluminescence (PL)) revealed that higher photogenerated charge carrier separation efficiency of iron-doped titania. Results showed that the 0.1 mol % Fe doped TiO_2 exhibited the highest photocatalytic activity for both degradation and H_2 evolution reactions.

Ahmad, Jaiswal and Soni (2020) has investigated the antibacterial and antifungal activity of the green synthesized TiO_2 NPs using leaf extract of *Mentha arvensis*, titanium tetraisopropoxide act as the precursor and leaf extract act as the reducing agent. The XRD study of the synthesized NPs shows the crystalline structure and the incidence of peaks at 25.27° corresponds to 110 anatase form. SEM study revealed that the synthesized NPs was spherical in shape and the average size of the synthesized NPs was found to be the range of 20-70 nm. Green synthesized TiO_2 NPs exhibited interesting antibacterial and antifungal activity against selected microorganism.

3. Research Gap Identification

In fact, many researchers have studied synthesis of TiO_2 and doped TiO_2 NPs by using different types of transition elements but there is very less literature on the synthesis of dual doped transition elements TiO_2 NPs and calcinated at particular temperature. The present study will discuss the comparative physiochemical properties of anatase phase of chemically and biologically synthesized dual doped TiO_2 NPs. In addition to this, synthesized NPs will be used for the photocatalytic and antioxidant activity.

4. Objectives

In the light of above discussions, the objectives of present study are as follows:

- To study chemically and biologically synthesis of anatase phase of dual doped transition elements TiO_2 NPs with microwave assisted method.

- Encapsulating polymer PVP and plant *T. Cordifolia* to chemically and biologically dual doped TiO_2 NPs, respectively.
- To characterize the synthesized dual doped TiO_2 NPs by using different characterization techniques like X-ray diffraction (XRD), Raman spectroscopy, UV-visible spectroscopy, Scanning electron microscope (SEM), Energy-dispersive X-ray spectroscopy (EDS) and Transmission electron microscope (TEM).
- To study the photocatalytic activity of synthesized NPs by using different commercial dyes.

5. Proposed Methodology

5.1 Materials

Ammonia solution (25 %, Emplura), Ascorbic acid (99 %, Labo), Cobalt (II) acetate tetrahydrate (98.5 %, Emplura), Copper (II) chloride dihydrate (98.5 %, Emplura), Ethanol (99.9 %), Methyl orange, Methylene blue, Nickle (II) chloride hexahydrate (97 %, Emplura), Polyvinylpyrrolidone (PVP-1,300,000), Titanium tetraisopropoxide (TTIP-97 %, Sigma Aldrich), Zinc acetate dihydrate (98 %, Emplura), 2,2-diphenyl-1-picrylhydrazyl (DPPH) and distilled water. Plant stems of *T. Cordifolia* will be collected from local areas of district Hamirpur, Himachal Pradesh for the preparation of extract.

5.2 Synthesis of *T. Cordifolia* plant extract

The fresh stem of *T. Cordifolia* plant will be collected from local areas of district Hamirpur, Himachal Pradesh. The collected stems will be washed properly with tap water and then with distilled water to remove the dust, microorganism, any particles or other impurities that may be on the stems. Washed stem will be weight accurately 10 gm. Further, well-minced stems will be boiled at temperature 70 ^{o}C for about 30-35 minutes in 100 ml distilled water. The assembly will consist of the attachment of the condenser with the round bottom flask standing on the rota-mantle with constant stirring. The boiled extract will be cooled and filtered through Whatman filter paper. The filtered extract solution will be used for the synthesis of dual doped TiO_2 NPs.

5.3 Synthesis of chemically and biologically dual doped TiO_2 NPs

Metal precursor solution of Titanium tetraisopropoxide with dopant transition elements at different concentrations at different concentrations will be prepared in the ethanol. A fixed volume of polymer PVP and plant extract *T. Cordifolia* will be encapsulated in above metal precursor solutions. Also, fixed volume of ammonia will be

added by dropwise addition with constant stirring for some time. After that deep internal homogenously, the reaction mixture will be placed in the microwave for certain time. Further, the prepared dual doped TiO_2 NPs will be centrifuged with distilled water and ethanol for 3-4 time and then dried in a vacuum oven at particular temperature. Finally, dual doped TiO_2 NPs will be calcinated at 400 ^oC temperature for 2-3 hours.

5.4 Characterization of chemically and biologically dual doped TiO_2 NPs

The chemically and biologically dual doped TiO_2 NPs will be characterized to determine its various physical as well as chemical properties such as crystallite size, crystal structure, lattice parameters, crystal phase, bandgap, surface morphology, elemental compositions and particle size. The characterization techniques will be used for determining these parameters are X-ray diffraction (XRD), Raman spectroscopy, UV-visible spectroscopy, Scanning electron microscope (SEM), Energy-dispersive X-ray spectroscopy (EDS) and Transmission electron microscope (TEM).

5.5. Photocatalytic activity

In this study, experiments will be performed to evaluate the photocatalytic properties of chemically and biologically dual doped TiO_2 NPs by photocatalytic degradation of commercial dyes. The photocatalytic decomposition of dyes will be examined by measuring the absorbance at regular time intervals by using UV-visible spectrophotometer.

5.6. Antioxidant activity

The chemically and biologically dual doped TiO_2 NPs will be used for the antioxidant activity by investigating the radical scavenging against stable free radical DPPH assay at different concentrations by using serial dilution. The antioxidant activity of the dual doped TiO_2 NPs against free radicals DPPH assay will be examined by measuring the absorbance using a UV-visible spectrophotometer.

6. Thesis Outline

The thesis will be comprised of following chapters:

Chapter 1 (Introduction): It will constitute of the brief account about nanotechnology, nanoparticles polymer PVP, plant *T. Cordifolia* and applications of TiO_2 NPs. It will also include the objectives of proposed study.

Chapter 2 (Literature Review): This chapter will deal with intense literature with context to the synthesis, characterization and applications of TiO_2 NPs. It will also include the research gap identification.

Chapter 3 (Materials and Methods): This chapter will comprise the detail of materials, chemically and biologically synthesis, characterization techniques and applications of dual doped TiO_2 NPs.

Chapter 4 (Results and Discussion): This chapter will include the reports regarding physiochemical properties and applications of chemically and biologically dual doped TiO_2 NPs along and comparison of the findings the work.

Chapter 5 (Summary and Conclusion): It will include the overall summary and conclusion of the entire study with regard to the work with context to the objectives cited.

Chapter 6 (References): This will include references which will be strictly according to the Harvard style.

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CERTIFICATE
(SYNOPSIS APPROVAL CERTIFICATE)

This is to certify that the Synopsis for Ph.D. Thesis titled, **"A study of chemically and biologically synthesized dual doped titanium dioxide (TiO_2) nanoparticles"**, submitted by **Mr. Nikesh Thakur** to the Career Point University, Hamirpur (H.P.), India in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY** in the Department of **Physics**, School of **Basic & Applied Sciences** has been approved by the Research Advisory Committee (RAC) after an Oral Examination of the student on dated 27.06.2022.

Dr. Naveen Thakur, Professor
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